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<b>(21) International Application Number:</b> PCT/US93/04785 <b>(22) International Filing Date:</b> 20 May 1993 (20.05.93)  <b>(30) Priority data:</b> 894,148                      4 June 1992 (04.06.92)                      US  <b>(71) Applicant:</b> OLIN CORPORATION [US/US]; 350 Knotter Drive, P.O. Box 586, Cheshire, CT 06410-0586 (US). <b>(72) Inventors:</b> SMITH, Curtis, P. ; 254 N. Rolling Acres, Cheshire, CT 06410 (US). REISCH, John, W. ; 52 Birch Drive, Guilford, CT 06437 (US). O'CONNOR, James, M. ; 107 Beckett Avenue, Branford, CT 06405 (US). <b>(74) Agents:</b> CARLSON, Dale, Lynn et al.; Olin Corporation, 350 Knotter Drive, P.O. Box 586, Cheshire, CT 06410-0586 (US).		<b>(81) Designated States:</b> AU, BB, BG, BR, CA, CZ, FI, HU, JP, KP, KR, KZ, LK, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> HARD THERMOPLASTIC POLYURETHANE ELASTOMERS  <b>(57) Abstract</b>  <p>This invention relates to a method of fabricating a thermoplastic elastomer which comprises the steps of: (a) fabricating a polyol blend having a desired polydispersity and comprising a first polyol and a second polyol, a diisocyanate, and a difunctional, isocyanato-reactive chain-extender, the first polyol being prepared utilizing a double metal cyanide complex catalyst and having a molecular weight of between about 1,000 and about 5,000, said first polyol having an end group unsaturation level of no greater than 0.04 milliequivalents per gram of polyol, the second polyol being a polyether polyol having an average molecular weight of between about 1,000 and about 20,000, (b) reacting said polyol blend with a diisocyanate to produce an isocyanate-terminated prepolymer, and (c) reacting said isocyanate-terminated prepolymer with a difunctional isocyanato-reactive chain extender in a mold or in an extruder in order to produce a hard elastomer characterized by a hardness of between a 75 Shore A and about a 75 Shore D. Also claimed is the elastomer produced by the above method utilizing a one-shot technique.</p>		

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## HARD THERMOPLASTIC POLYURETHANE ELASTOMERS

The present invention relates generally to the production of thermoplastic polyurethane ("TPU") elastomers and polyurea elastomers having high hardness and, more specifically, to the production of elastomers  
5 utilizing a polyol blend containing a low unsaturation level polyol prepared using a double metal cyanide complex catalyst.

The use of double metal cyanide (so-called "DMC") catalysts in the preparation of high molecular weight  
10 polyols is well-established in the art. For example, U.S. Patent 3,829,505, assigned to General Tire & Rubber Company, discloses the preparation of high molecular weight diols, triols etc., using these catalysts. The polyols prepared using these catalysts can be fabricated  
15 to have a higher molecular weight and a lower amount of end group unsaturation than can be prepared using commonly-used KOH catalysts. The '505 patent discloses that these high molecular weight polyol products are useful in the preparation of nonionic surface active  
20 agents, lubricants and coolants, textile sizes, packaging films, as well as in the preparation of solid or flexible polyurethanes by reaction with polyisocyanates.

Certain thermoset polyurethane elastomers  
25 produced using triols made by DMC catalysis are also known. More specifically, U.S. Patent 4,242,490

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discloses the preparation of such elastomers by reacting a DMC catalyst-prepared polypropylene ether triol having a molecular weight of from 7,000 to 14,000, ethylene glycol, and toluene diisocyanate in a specified range of molar ratios using either a prepolymer process or a "one-shot" process.

Methodology for preparing TPU elastomers is well-established in the art. By way of illustration, U.S. Patent 4,202,957 discloses polyurethane polyether-based elastomers, made using a select group of polypropylene oxide-polyethylene oxide block copolymers, which this patent states are thermoplastic, recyclable and possess high temperature degradation resistance thus permitting fabrication by injection molding.

As another illustration, U.S. Patent 5,096,993 discloses the production of TPU elastomers made using DMC-prepared polyether polyols. These elastomers are disclosed in the '993 patent as having excellent physical and chemical properties.

Unfortunately, hard TPU elastomers, such as those elastomers having a hardness within the range of between 75 Shore A and about 75 Shore D, prepared in accordance with prior art methods utilizing a DMC-prepared polyol are generally not as readily extruded into shaped articles as might be desired. Accordingly, new methodology for producing hard elastomers having excellent physical and chemical properties made using DMC-prepared polyol(s) in a readily extrudable elastomer-forming composition would be highly desired by the elastomer manufacturing community. The present invention provides such desired methodology.

In one aspect, the present invention relates to a thermoplastic polyurethane or polyurea elastomer made by reacting in a "one-shot" process (preferably a

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continuous one-shot process) a polyol blend of polyether polyols comprising a first polyol and a second polyol, a diisocyanate, and a difunctional, isocyanato-reactive chain-extender, the first polyol being prepared

5 utilizing a double metal cyanide complex catalyst and having a molecular weight of between about 1,000 and about 5,000 (advantageously between 1,500 and 4,000, more advantageously between 1,500 and 2,500), said first polyol having an end group unsaturation level of no

10 greater than 0.04 (preferably less than 0.02, more preferably less than 0.01) milliequivalents per gram of polyol, the second polyol being a polyether polyol having an average molecular weight of between about 1,000 and about 20,000 (advantageously between 1,000 and

15 4,000, more advantageously between 1,000 and 4,000), the second polyol being present in an amount of between about 5% and about 50% based upon the weight of said polyol blend, with the proviso that the average molecular weight of said second polyol is different from

20 the average molecular weight of said first polyol, and with the additional proviso that the polydispersity of said polyol blend is greater than the polydispersity of said first polyol, the polydispersity of said polyol blend being between about 1.05 and about 3.0 (preferably

25 between 1.1 and 1.5, more preferably between 1.1 and 1.2), the equivalent ratio of NCO groups on said diisocyanate to active hydrogen groups on said polyol plus chain extender being between about 1:0.7 and about 1:1.3 (preferably between 1:0.9 and 0.9:1, more

30 preferably between 1:0.95 and 0.95:1), and the molar ratio of chain extender to polyol being between about 0.15:1 and about 75:1, said elastomer having a hardness of between a 75 (preferably at least 80) Shore A and about a 75 (preferably no greater than 65, more

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preferably no greater than 55) Shore D. Preferably, the first polyol and the second polyol are each polyether diols.

In another aspect, the present invention relates  
5 to a thermoplastic polyurethane or polyurea elastomer made by reacting an isocyanate-terminated prepolymer with a difunctional isocyanato-reactive chain-extender, the isocyanate-terminated prepolymer being the reaction product of a polyisocyanate and a polyol blend of  
10 polyether polyols comprising a first polyol and a second polyol, the first polyol being prepared utilizing a double metal cyanide complex catalyst and having a molecular weight of between about 1,000 and about 5,000 (advantageously between 1,500 and 4,000, more  
15 advantageously between 1,500 and 2,500), said first polyol having an end group unsaturation level of no greater than 0.04 (preferably less than 0.02, more preferably less than 0.01) milliequivalents per gram of polyol, the second polyol being a polyether polyol  
20 having an average molecular weight of between about 1,000 and about 20,000 (advantageously between 1,000 and 4,000, more advantageously between 1,000 and 4,000), the second polyol being present in an amount of between about 5% and about 50% based upon the weight of said  
25 polyol blend, with the proviso that the average molecular weight of said second polyol is different from the average molecular weight of said first polyol, and with the additional proviso that the polydispersity of said polyol blend is greater than the polydispersity of  
30 said first polyol, the polydispersity of said polyol blend being between 1.09 and about 3.0 (preferably between 1.1 and 1.5, more preferably between 1.1 and 1.2), the equivalent ratio of NCO groups on said diisocyanate to active hydrogen groups on said polyol

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plus chain extender being between about 1:0.7 and about 1:1.3 (preferably between 1:0.9 and 0.9:1, more preferably between 1:0.95 and 0.95:1), and the molar ratio of chain extender to polyol being between about 5 0.15:1 and about 75:1, said elastomer having a hardness of between a 75 (preferably at least 80) Shore A and about a 75 (preferably no greater than 65, more preferably no greater than 55) Shore D. Preferably, the first polyol and the second polyol are each polyether 10 diols.

In yet another aspect, the present invention relates to a method of fabricating a thermoplastic elastomer which comprises the steps of:

(a) fabricating a polyol blend of polyether 15 polyols comprising a first polyol and a second polyol, the first polyol being prepared utilizing a double metal cyanide complex catalyst and having a molecular weight of between about 1,000 and about 5,000 (advantageously between 1,500 and 4,000, more advantageously between 20 1,500 and 2,500), said first polyol having an end group unsaturation level of no greater than 0.04 (preferably less than 0.02, more preferably less than 0.01) milliequivalents per gram of polyol, the second polyol being a polyether polyol having an average molecular 25 weight of between about 1,000 and about 20,000 (advantageously between 1,000 and 4,000, more advantageously between 1,000 and 4,000), the second polyol being present in an amount of between about 5% and about 50% based upon the weight of said polyol 30 blend, with the proviso that the average molecular weight of said second polyol is different from the average molecular weight of said first polyol, and with the additional proviso that the polydispersity of said polyol blend is greater than the polydispersity of said

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first polyol, the polydispersity of said polyol blend being between about 1.05 and about 3.0 (preferably between 1.1 and 1.5, more preferably between 1.1 and 1.2),

5 (b) reacting said polyol blend with a diisocyanate to produce an isocyanate-terminated prepolymer, and

(c) reacting said isocyanate-terminated prepolymer with a difunctional isocyanato-reactive chain  
10 extender in a mold or in an extruder in order to produce a hard elastomer characterized by a hardness of between a 75 (preferably at least 80) Shore A and about a 75 (preferably no greater than 65, more preferably no greater than 55) Shore D, with the proviso that when the  
15 molecular weight of the polyol is less than 4,000, then the polyol has an ethylene oxide content of less than 35 weight based upon the weight of the polyol. Preferably, the polyol blend has an average ethylene oxide ("EO") content as a cap of between about 0% and about 45%,  
20 preferably between 5% and 30%, more preferably between 10% and 25%, based upon the total weight of the polyol blend. Preferably, the first polyol and the second polyol are each polyether diols.

These and other aspects will become apparent upon  
25 reading the following detailed description of the invention.

It has now been surprisingly found that hard, readily extrudable thermoplastic elastomers having a hardness in the range of between a 75 Shore A and a 75  
30 Shore D, and fabricated using at least one polyol made using a DMC catalyst, are suitably produced in accordance with the present invention. The elastomers are produced utilizing a polyol blend containing at least one polyol prepared using a double metal cyanide



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complex catalyst. These elastomers exhibit excellent physical and chemical properties. The elastomers possess excellent structural strength and stability characteristics. In addition, the elastomers are  
5 recyclable and can be re-extruded and remolded if desired.

The present invention is particularly surprising because previous efforts to produce such hard elastomers by the present inventors using made with a DMC catalyst  
10 have resulted in poorly extrudable elastomers-forming polymers which tend to "slam-up" or crystallize in colder portions of the extruder or die during extrusion processing. Instead of the desired clear, transparent, extruded film one obtains an undesired hazy, milky film  
15 that may contain random chunks of hard material. Without wishing to be bound to any particular theory, it is believed by the present inventors that such poor extrudability is attributable to the narrow molecular weight distribution of polyols made using DMC  
20 catalysts. The present invention provides a solution to this extrudability problem, and this solution is believed to be attributable to the enhanced molecular weight distribution or polydispersity associated with the polyols employed in the present invention.

25 The thermoplastic elastomers of the present invention may be made by the prepolymer process or the one-shot process. The polyurethane isocyanate-terminated prepolymer that is utilized when employing the prepolymer process according to the invention is  
30 prepared by reacting an organic polyisocyanate with a polyalkylene ether polyol(s) in an equivalent ratio of NCO to OH groups of from about 15:1 and about 1.2:1 (preferably between 7:1 and 3:1), using standard procedures, to yield an isocyanate-terminated prepolymer

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of controlled molecular weight. The reaction may be accelerated by employing a catalyst; common urethane catalysts are well known in the art and include numerous organometallic compounds as well as amines, e.g.,  
5 tertiary amines and metal compounds such as lead octoates, mercuric succinates, stannous octoate or dibutyltin dilaurate may be used. Any catalytic amount may be employed; illustratively, such amount varies, depending on the particular catalyst utilized, from  
10 about 0.01 to about 2 percent by weight of the polyurethane prepolymer.

The polyol blend comprises at least a first polyol and a second polyol, and additional polyols may be employed in the blend as desired. The preferred  
15 polyol blends consist essentially of two or three polyols. Preferred polyol reactants are the polyether diols and combinations thereof. Suitable polyether diols include various polyoxyalkylene diols and combinations thereof, preferably containing ethylene  
20 oxide ("EO") in an amount of between about 5 and about 40, more preferably between about 15 and about 30, weight percent based upon the weight of the polyol. Suitable diols preferably have a primary hydroxyl  
25 preferably between about 50 and about 95%. The ethylenic unsaturation level for the polyol is preferably no greater than 0.04, more preferably less than 0.025, milliequivalents per gram of polyol. It is preferred that any residual alkali metal catalyst in the  
30 polyol be no greater than 25 ppm, more preferably no greater than 8 ppm, most preferably no greater than 5 ppm. The potential adverse effects of residual alkali metal catalyst in the polyol can be overcome by

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neutralizing with an effective amount of an acid, such as phosphoric acid.

The polyols can be prepared, according to well-known methods, by condensing an alkylene oxide, or  
5 a mixture of alkylene oxides using random or step-wise addition, with a polyhydric initiator or mixture of initiators. Illustrative alkylene oxides include ethylene oxide, propylene oxide, butylene oxide, amylene oxide, aralkylene oxides such as styrene oxide, and the  
10 halogenated alkylene oxides such as trichlorobutylene oxide and so forth. The most preferred alkylene oxide is propylene oxide or a mixture thereof with ethylene oxide using random or step-wise oxyalkylation.

The polyhydric initiator used in preparing the  
15 polyether diol reactant includes the following and mixtures thereof: ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, butylene glycol, butane diols, pentane diols, water, combinations thereof, and the like.

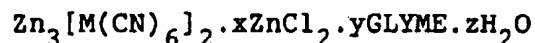
20 The alkylene oxide-polyhydric initiator condensation reaction is preferably carried out in the presence of a double metal cyanide catalyst. Without wishing to be bound by any particular theory, it is speculated by the present inventor that unsaturated end  
25 groups result in monofunctional species that act as chain stoppers in elastomer formation. In polyol synthesis with KOH catalysis, the unsaturation formed increases as a direct function of equivalent weight. Eventually conditions are established wherein further  
30 propylene oxide addition fails to increase the molecular weight. In other words, the use of alkali catalysts to produce high molecular weight, hydroxy terminated polyoxypropylene ethers results in a substantial loss in hydroxy functionality. With double metal cyanide

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catalysis, much less unsaturation is formed allowing higher equivalent weight polyols to be prepared.

The double metal cyanide complex class catalysts suitable for use and their preparation are described in  
5 U.S. Pat. Nos. 4,472,560 and 4,477,589 to Shell Chemical Company and U.S. Pat. Nos. 3,941,849; 4,242,490 and 4,335,188 to The General Tire & Rubber Company.

One double metal cyanide complex catalyst found particularly suitable for use is a zinc  
10 hexacyanometallate of formula:



wherein M may be Co(III), or Cr(III) or Fe(II) or Fe(III); x, y, and z may be fractional numbers, integers, or zero and vary depending on the exact method  
15 of preparation of the complex.

The second component of the polyol blend having a different molecular weight, either higher or lower or a mixture of both high and low, in order to widen the molecular weight distribution. A measure of the  
20 molecular weight distribution, polydispersity, is measured on a suitable GPC or HPSEC column or set of columns and is related to the ratio of the weight-average molecular weight and the number-average molecular weight,  $M_w/M_n$ . A  $M_w/M_n$  of 1.054 or  
25 lower does not allow the formation of a suitable extrusion grade polymer while a  $M_w/M_n$  between 1.054 and 3.5 (preferably between 1.10 and 3.0, more preferably between 1.10 and 2.5) yields desirable materials.

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Any suitable organic diisocyanate, or mixture of diisocyanates, may be used in the elastomer-forming process of the present invention. Illustrative are toluene diisocyanate, such as the 80:20 and the 65:35 mixtures of the 2,4- and 2,6-isomers, ethylene diisocyanate, propylene diisocyanate, methylene-bis (4-phenyl) isocyanate (also referred to as diphenylmethane diisocyanate or MDI), dibenzyl diisocyanate, xylene diisocyanate (XDI), isophorone diisocyanate (IPDI), 3,3'-bistoluene-4,4'-diisocyanate, hexamethylene diisocyanate (HDI), hydrogenated MDI, hydrogenated XDI, cyclohexane diisocyanate, paraphenylene diisocyanate, mixtures and derivatives thereof, and the like. Other advantageous embodiments of the invention suitably employ an isomeric mixture of 2,4- and 2,6-toluene diisocyanate in which the weight ratio of the 2,4-isomer to the 2,6-isomer is from about 60:40 to about 90:10, and more preferably from about 65:35 to about 80:20, as well as MDI.

Chain extenders useful in the present invention include diols and diamines such as ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, butane diol, pentane diol, 3-methylpentane-1,5-diol, hexane diol, oxyalkylated hydroquinone, resorcinol and bisphenol A, hydrogenated bisphenol A, 1,4-cyclohexane dimethanol, or polyalkylene oxide diols with molecular weights between 100 - 500, diethyltoluene diamine, ethylene diamine, 4,4'-methylene bis(2-chloroaniline) ("MOCA"), hydrazine, substituted aromatic diamines such as the product commercially available as UNILINK 4200, a product of UOP, Inc., N,N-bis(2-hydroxypropyl)-aniline which is commercially available as ISONOL 100, a product of Dow Chemical Corp., and the like, and combinations thereof. The chain extension can be conducted either in

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situ during the prepolymer formation or in a separate reaction step.

In preparing the polyurethane and/or polyurea elastomer, the polyether polyol(s), polyisocyanate(s), chain extender(s), and other components are reacted, typically under conditions of an elevated temperature. A preferred method of forming the desired thermoplastic elastomers is by continuous processing utilizing an extruder as illustrated by U.S. Patent 3,642,964. An alternative method involves batch processing, followed by grinding and extrusion of the formed elastomer as is well-known in the art. Although either the prepolymer method or the one-shot method can be used, the one-shot method is preferred. The one-shot method is intended to also include the process whereby the diisocyanate has been converted to a quasi-prepolymer by reaction with a minor amount (i.e., less than about 10 percent on an equivalent basis) of polyol prior to carrying out the polyurethane forming reaction.

In preparing the elastomer, urethane forming catalysts can be used as well as the usual compounding ingredients such as antioxidants or other antidegradants. Typical antioxidants include hindered phenols, butylated hydroxytoluene ("BHT"), and the like. Other optional compounding ingredients include, for example, plasticizers, adhesion promoters, fillers and pigments like clay, silica, fumed silica, carbon black, talc, phthalocyanine blue or green, TiO<sub>2</sub>, U-V absorbers, MgCO<sub>3</sub>, CaCO<sub>3</sub> and the like. The compounding ingredients, such as fillers, are suitably employed in the elastomer in an amount of between 0 and about 75 weight percent based upon the weight of the elastomer. The polymerization reaction may be carried out in a

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single reaction (one-shot process), or in one or more sequential steps (prepolymer process), using either bulk polymerization or solution polymerization. When solution polymerization is used, polar solvents such as tetrahydrofuran ("THF"), dimethylformamide ("DMF"), and dimethylacetamide ("DMAC") are typically utilized. In the one-shot process, all the isocyanate-reactive components are reacted simultaneously with the polyisocyanate. In such process, it is normal practice to blend all components except the polyisocyanate into a "B-side" mixture, which is then reacted with the polyisocyanate to form the polyurethane and/or polyurea elastomer. However, the order of mixing is not critical as long as the components do not undesirably react before all components are present. The reaction mixture is usually then placed in a mold, or extruded through an extruder, and cured at a suitable temperature. The apparatus used for blending and molding is not especially critical. Hand mixing, conventional machine mixing, and the so-called reaction injection molding (RIM) equipment are all suitable. In the prepolymer process, all or a portion of one or more of the isocyanate reactive materials is reacted with a stoichiometric excess of the polyisocyanate to form an isocyanate-terminated prepolymer. This prepolymer is then allowed to react with the remaining isocyanate-reactive materials to prepare the polyurethane and/or polyurea elastomer. The prepolymer can be prepared with either the polyether or the chain extender, or a mixture of both.

The mixing of the reactants can be carried out at ambient temperature (of the order of 25°C.) and the resulting mixture is then heated to a temperature of the order of about 40°C. to about 130°C., preferably to a

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temperature of about 90°C. to about 120°C Alternatively,  
and preferably, one or more of the reactants is  
preheated to a temperature within the above ranges  
before the admixing is carried out. Advantageously, in  
5 a batch procedure, the heated reaction components are  
subjected to degassing in order to remove entrained  
bubbles of air, water, or other gases before the  
reaction takes place. This degassing is accomplished  
conveniently by reducing the pressure under which the  
10 components are maintained until no further evolution of  
bubbles occurs. The degassed reaction components are  
then admixed and transferred to suitable molds or  
extrusion equipment or the like and cured at a  
temperature of the order of about 20°C. to about 115°C.  
15 The time required for curing will vary the temperature  
of curing and also with the nature of the particular  
composition, as is known in the art.

As used herein, the terms "molecular weight" and  
"average molecular weight" are intended to designate  
20 weight average molecular weight. "Polydispersity" is  
defined as the weight-average molecular weight divided  
by the number-average molecular weight.

While the invention has been described above with  
reference to specific embodiments thereof, it is  
25 apparent that many changes, modifications and variations  
can be made without departing from the inventive concept  
disclosed herein. Accordingly, it is intended to  
embrace all such changes, modifications and variations  
that fall within the spirit and broad scope of the  
30 appended claims.



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## SPECIFIC EXAMPLES

## I. PREPARATION OF HIGH MOLECULAR WEIGHT POLYOL WITH LOW UNSATURATION

A 2 gallon autoclave was filled with 550 g. of  
5 POLY-G\* 20-112, a polyoxypropylene diol of molecular  
weight 1000, and 2.2 g. of a double metal cyanide  
catalyst. The catalyst is a Zinc Cobaltihexacyanate  
complex with 1,2-dimethoxyethane (glyme). The reactor  
was closed, flushed three times with nitrogen and then  
10 heated to 100°C. At that time a total of 150 g.  
propylene oxide was added and after 20 min. the reaction  
started, as evidenced by a pressure drop. Then  
propylene oxide, 3850 g. was added over a period of 4  
hrs at a propylene oxide partial pressure of 30 psi.  
15 When the pressure dropped to 10 psi. KOH, 16 g.,  
was introduced into the reactor and then ethylene oxide,  
680 g., was allowed to react at 70 psi for 5 hrs. The  
unreacted ethylene oxide was vented and the reactor  
cooled and opened up. To the reactor was added  
20 magnesium silicate, 100 g., and Supercell filter aid,  
100 g. The contents of the autoclave were then heated  
to 100°C for 2 hrs., after which time a vacuum of 25"  
water was applied for 1 hr. The polyol was then pushed  
through a small preheated filter press, containing a 5  
25 micron paper filter, at 40 psi. and 100°C. Analysis  
showed that the polyol contained 9% ethylene oxide, had  
an OH # of 16 mg KOH/g. and had 70% primary OH. The  
unsaturation value was 0.0175 meq/g. and the Zn, Co and  
K contents were below 2 ppm.

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II. PREPARATION OF A 4000 MOLECULAR WEIGHT LOW  
UNSATURATION CONTAINING POLYOL (OH# 28.3, MW 3965)

In a preparation similar to I. above a polyol  
was prepared where analysis showed that the material  
5 contained 20% ethylene oxide and had an OH # of 28.3 mg  
KOH/g. The unsaturation value was 0.005 meq/g. and the  
residual KOH was 0.0 ppm.

III. PREPARATION OF A 2000 MOLECULAR WEIGHT LOW  
UNSATURATION CONTAINING POLYOL (OH# 50.1 MW 2240)

10 In a preparation similar to I. above a polyol  
was prepared where analysis showed that the material  
contained 24.6% ethylene oxide, 75.6% primary OH and had  
an OH # of 50.1 mg KOH/g. The unsaturation value was  
0.007 meq/g. and the KOH residue was 0.20 ppm.

15 PREPARATION OF A THERMOPLASTIC POLYURETHANE - 30% Hard  
Segment

A 2000 ml resin flask was charged with 1100 g.,  
0.491 moles, of the polyol (OH# 50.1). In addition,  
1,4-butanediol, 138.8 g., 1.54 mole, and less than 1 wt%  
20 of a mixture of phenolic antioxidant, ester mold release  
and other processing aids were added. The mixture was  
dehydrated at 85°C in vacuo, 1-2 mm Hg, for two hours  
after which time period 300 g. increments were weighed  
out and placed in a 90°C oven prior to mixing with the  
25 isocyanate.

Reaction with Diphenylmethane Diisocyanate

Diphenylmethane diisocyanate, MDI, 125.5 g.,  
0.502 mole, increments were weighed out and maintained  
at 90°C prior to mixing. To prepare the thermoplastic

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polyurethane stannous octoate, 0.14-0.18 g. were added to the polyol samples and mixed. The MDI was then added and the mixture rapidly stirred until it thickens (10-15 sec) at which point it is then poured into a Teflon\* coated pan and allowed to cure. After curing the elastomer is granulated, dried at 100°C and 0.3 mm Hg for 14-18 hrs.

The dried polymer is compression molded at 420°F. Specimens for tensile, die C and split tear were die cut from the molded plaques after standing 5 days at ambient temperature. An elastomer of 79 Shore A hardness and 5512 psi tensile strength is obtained.

The dried polymer is extruded in a 3/4" extruder through a 4" film die at a profile of: zone 1, 195°C; zone 2, 202°C; zone 3, 203°C; die, 209°C. The resulting cloudy tape has 300% modulus of 1200 psi and ultimate tensile strength of 4500 psi.

#### PREPARATION OF A THERMOPLASTIC POLYURETHANE - 35% Hard Segment

A 2000 ml resin flask was charged with 1200 g., 0.536 moles, of vacuum dried polyol (OH# 50.1). In addition, 1,4-butanediol, 190.2 g., 2.11 mole, and less than 1 wt% of a mixture of phenolic antioxidant, ester mold release and other processing aids were added. The mixture was dehydrated at 85°C in vacuo, 1-2 mm Hg, for two hours after which time period 300 g. increments were weighed out and placed in a 90°C oven prior to mixing with the isocyanate.

#### Reaction with Diphenylmethane Diisocyanate

Diphenylmethane diisocyanate, MDI, 157.9 g., 0.631 mole, increments were weighed out and maintained

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at 90°C prior to mixing. To prepare the thermoplastic polyurethane stannous octoate, 0.05-0.10 g. were added to the polyol samples and mixed. The MDI was then added and the mixture rapidly stirred until it thickens (10-18  
5 sec) at which point it is then poured into a Teflon\* coated pan and allowed to cure. After curing the elastomer is granulated, dried at 100°C and 0.3 mm Hg for 14-18 hrs.

The dried polymer is compression molded at  
10 420-430°F. The plaques were hazy and appeared to be inhomogeneous, with areas of clear polymer and areas of white, opal.

The dried polymer is extruded in a 3/4" extruder through a 4" film die at a profile of: zone 1, 190°C;  
15 zone 2, 195°C; zone 3, 195°C; die, 208°C. After a short extrusion period, where a cloudy, white tape resulted, the material crystallized in the barrel of the extruder. Starting with a profile of: zone 1, 190°C; zone 2, 200°C; zone 3, 200°C; die, 212°C the melt  
20 viscosity is too low to allow a film to form.

#### PREPARATION OF POLYOL BLENDS

The polyol blends listed in Table 1 were made by mixing the indicated parts by weight of the different polyols and then determining the hydroxyl number (OH#),  
25 weight average molecular weight ( $M_w$ ) and polydispersity ( $M_w/M_n$ ) of the polyol blend prior to making the thermoplastic polyurethanes. The polydispersity was measured by GPC chromatography, whereas the molecular weight of the blend was calculated  
30 based upon the hydroxyl numbers of the individual polyols (polyols A, B, and C) employed in producing the various polyol blends.

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TABLE 1. Polyol Blends - Parts by Weight

	<u>Individual Polyol</u>			<u>Blend Characteristics</u>		
	A	B	C			
Polyol	OH#	OH#	OH#	OH# of	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>
5 Blend	112.7*	50.1	27.9	Blend		
I	0	100	0	50.1	2240	1.054
II	10	90	0	57.7	1944	1.106
III	20	80	0	57.2	1962	1.165
IV	0	90	10	48.5	2313	1.091
10 V	0	80	20	46.6	2408	1.165
VI	5	90	5	54.4	2062	1.103
VII	10	80	10	54.2	2070	1.173

\* Polyol made by conventional (KOH) catalysis, not DMC catalysis

#### 15 PREPARATION OF A THERMOPLASTIC POLYURETHANE - 35% Hard Segment - Polyol Blend V

A 2000 ml resin flask was charged with 1100 g. of the polyol blend V and vacuum dried polyol. In addition, 1,4-butanediol, 173.1 g., 1.92 mole, and less  
 20 than 1 wt% of a mixture of phenolic antioxidant, ester mold release and other processing aids were added. The mixture was dehydrated at 85°C in vacuo, 1-2 mm Hg, for two hours after which time period 300 g. increments were weighed out and placed in a 90°C oven prior to mixing  
 25 with the isocyanate.

#### Reaction with Diphenylmethane Diisocyanate

Diphenylmethane diisocyanate, MDI, 143.0 g., 0.571 mole, increments were weighed out and maintained

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at 90°C prior to mixing. To prepare the thermoplastic polyurethane stannous octoate, 0.05-0.10 g. were added to the polyol samples and mixed. The MDI was then added and the mixture rapidly stirred until it thickens (18-26  
5 sec) at which point it is then poured into a Teflon\* coated pan and allowed to cure. After curing the elastomer is granulated, dried at 100°C and 0.3 mm Hg for 14-18 hrs.

The dried polymer is compression molded at  
10 400°F. Specimens for tensile, die C and split tear were die cut from the molded plaques after standing 5 days at ambient temperature. An elastomer of 87 Shore A hardness and 6000 psi tensile strength is obtained.

The dried polymer is extruded in a 3/4" extruder  
15 through a 4" film die at a profile of: zone 1, 206°C; zone 2, 212°C; zone 3, 212°C; die, 215°C. The resulting nice clear tape has 300% modulus of 1630 psi and ultimate tensile strength of 5300 psi.

In a similar manner thermoplastic polyurethanes  
20 at 35% hard segment levels were made from the other polyol blends resulting in nice, clear extruded tapes and clear compression molded plaques. The physical property data is summarized in the Table 2.

#### PROPOSED EXAMPLES:

25 Example I. A blend of 50 parts polyol with OH# 112.7 and 50 parts OH# 50.1 gives a polyol with OH# 81.4.

#### PREPARATION OF A THERMOPLASTIC POLYURETHANE - 35% Hard Segment

A 2000 ml resin flask was charged with 950 g. of  
30 the polyol blend and vacuum dried polyol. In addition, 1,4-butanediol, 160.0 g., 1.78 mole, and less than 1 wt%

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of a mixture of phenolic antioxidant, ester mold release and other processing aids were added. The mixture was dehydrated at 85°C in vacuo, 1-2 mm Hg, for two hours after which time period 300 g. increments were weighed out and placed in a 90°C oven prior to mixing with the isocyanate.

#### Reaction with Diphenylmethane Diisocyanate

Diphenylmethane diisocyanate, MDI, 170.0 g., 0.680 mole, increments were weighed out and maintained at 90°C prior to mixing. To prepare the thermoplastic polyurethane stannous octoate, 0.05-0.10 g. were added to the polyol samples and mixed. The MDI was then added and the mixture rapidly stirred until it thickens (18-26 sec) at which point it is then poured into a Teflon\* coated pan and allowed to cure. After curing the elastomer is granulated, dried at 100°C and 0.3 mm Hg for 14-18 hrs.

The dried polymer is compression molded at 400°F. Specimens for tensile, die C and split tear were die cut from the molded plaques after standing 5 days at ambient temperature. An elastomer of 85-95 Shore A hardness and 6000 psi tensile strength is obtained.

The dried polymer is extruded in a 3/4" extruder through a 4" film die at a profile of: zone 1, 200-210°C; zone 2, 205-215°C; zone 3, 205-215°C; die, 205-220°C. The resulting nice clear tape has 300% modulus of 1500-2500 psi and ultimate tensile strength of 5000-6500 psi.

Example II. A blend of 50 parts polyol with OH# 50.1 and 50 parts OH# 27.9 gives a polyol with OH# 39.

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# PREPARATION OF A THERMOPLASTIC POLYURETHANE - 35% Hard Segment

A 2000 ml resin flask was charged with 950 g. of the polyol blend and vacuum dried polyol. In addition, 5 1,4-butanediol, 147.2 g., 1.63 mole, and less than 1 wt% of a mixture of phenolic antioxidant, ester mold release and other processing aids were added. The mixture was dehydrated at 85°C in vacuo, 1-2 mm Hg, for two hours after which time period 300 g. increments were weighed 10 out and placed in a 90°C oven prior to mixing with the isocyanate.

## Reaction with Diphenylmethane Diisocyanate

Diphenylmethane diisocyanate, MDI, 137.0 g., 0.548 mole, increments were weighed out and maintained 15 at 90°C prior to mixing. To prepare the thermoplastic polyurethane stannous octoate, 0.05-0.10 g. were added to the polyol samples and mixed. The MDI was then added and the mixture rapidly stirred until it thickens (18-26 sec) at which point it is then poured into Teflon\* 20 coated pan and allowed to cure. After curing the elastomer is granulated, dried at 100°C and 0.3 mm Hg for 14-18 hrs.

The dried polymer is compression molded at 400°F. Specimens for tensile, die C and split tear were 25 die cut from the molded plaques after standing 5 days at ambient temperature. An elastomer of 80-90 Shore A hardness and 5000-6000 psi tensile strength is obtained.

The dried polymer is extruded in a 3/4" extruder through a 4" film die at a profile of: zone 1, 30 200-210°C; zone 2, 205-215°C; zone 3, 205-215°C; die, 205-220°C. The resulting nice clear tape has 300%



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modulus of 1500-2500 psi and ultimate tensile strength of 5000-6500 psi.

## SUMMARY OF PHYSICAL PROPERTIES

## Extrusion:

	Polyol Blend	300% Modulus	Ultimate Tensile(psi)	Ultimate Elong.(%)
5	II	1575	6557	623
	III	1540	6140	660
	IV	1597	4238	675
	V	1631	5307	595
10	VI	1675	5871	630
	VII	1529	5201	640

## Compression Molded:

	Polyol Blend	Hardness	300% Modulus	Ultimate Tensile	Ultimate Elong(%)
15	II	86 A	2010	6117	680
	III	89 A	1876	4957	680
	IV	88 A	1991	5766	640
	V	87 A	1916	6011	677
	VI	88 A	1863	4696	705
20	VII	88 A	1792	4556	717

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WHAT IS CLAIMED IS:

1. A thermoplastic polyurethane or polyurea elastomer characterized by being made by reacting in a "one-shot" process a polyol blend of polyether polyols  
5 comprising a first polyol and a second polyol, a diisocyanate, and a difunctional, isocyanato-reactive chain-extender, the first polyol being prepared utilizing a double metal cyanide complex catalyst and having a molecular weight of between about 1,000 and  
10 about 5,000, said first polyol having an end group unsaturation level of no greater than 0.04 milliequivalents per gram of polyol, the second polyol being a polyether polyol having an average molecular weight of between about 1,000 and about 20,000, the  
15 second polyol being present in an amount of between about 5% and about 50% based upon the weight of said polyol blend, with the proviso that the average molecular weight of said second polyol is different from the average molecular weight of said first polyol, and  
20 with the additional proviso that the polydispersity of said polyol blend is greater than the polydispersity of said first polyol, the polydispersity of said polyol blend being between 1.09 and about 3.0, the equivalent ratio of NCO groups on said diisocyanate to active  
25 hydrogen groups on said polyol plus chain extender being between about 1:0.7 and about 1:1.3, and the molar ratio of chain extender to polyol being between about 0.15:1 and about 75:1, said elastomer having a hardness of between a 75 Shore A and about a 75 Shore D.
- 30 2. The elastomer of claim 1 characterized in that said chain extender is selected from the group consisting of diols, diamines, and combinations thereof.

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3. The elastomer of claim 1 characterized in that said chain extender is selected from the group consisting of ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, butane diol, 5 pentane diol, 3-methylpentane-1,5-diol, hexane diol, oxyalkylated hydroquinone, resorcinol and bisphenol A, hydrogenated bisphenol A, 1,4-cyclohexane dimethanol, polyalkylene oxide diols with molecular weights between 100 - 500, diethyltoluene diamine, ethylene diamine, 10 4,4'-methylene bis(2-chloroaniline) ("MOCA"), hydrazine, substituted aromatic diamines, N,N-bis(2-hydroxypropyl)-aniline, and combinations thereof.

4. The elastomer of claim 1 characterized in that said elastomer additionally contains at least one 15 compounding ingredient selected from the group consisting of anti-oxidants, plasticizers, uv stabilizers, adhesion promoters, fillers and pigments and employed in an amount of between 0 and about 75 weight percent based upon the total weight of the 20 composition.

5. The elastomer of claim 1 characterized in that said first polyol has a molecular weight of between 1,500 and 4,000 and said polyol blend has a polydispersity of between 1.1 and 1.5.

25 6. The elastomer of claim 1 characterized in that said polyol blend has an average ethylene oxide content of less than 35 weight percent if the average molecular weight of said polyol blend is less than 4,000.

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7. A thermoplastic polyurethane or polyurea elastomer characterized by being made by reacting an isocyanate-terminated prepolymer with a difunctional isocyanato-reactive chain-extender, the

5 isocyanate-terminated prepolymer being the reaction product of a polyisocyanate and a polyol blend of polyether polyols comprising a first polyol and a second polyol, the first polyol being prepared utilizing a double metal cyanide complex catalyst and having a

10 molecular weight of between about 1,000 and about 5,000, said first polyol having an end group unsaturation level of no greater than 0.04 milliequivalents per gram of polyol, the second polyol being a polyether polyol having an average molecular weight of between about

15 1,000 and about 20,000, the second polyol being present in an amount of between about 5% and about 50% based upon the weight of said polyol blend, with the proviso that the average molecular weight of said second polyol is different from the average molecular weight of said

20 first polyol, and with the additional proviso that the polydispersity of said polyol blend is greater than the polydispersity of said first polyol, the polydispersity of said polyol blend being between 1.09 and about 3.0, the equivalent ratio of NCO groups on said diisocyanate

25 to active hydrogen groups on said polyol plus chain extender being between about 1:0.7 and about 1:1.3, and the molar ratio of chain extender to polyol being between about 0.15:1 and about 75:1, said elastomer having a hardness of between a 75 Shore A and about a 75

30 Shore D.

8. The elastomer of claim 7 characterized in that said chain extender is selected from the group consisting of diols, diamines, and combinations thereof.

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9. The elastomer of claim 7 characterized in that said chain extender is selected from the group consisting of ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, butane diol, 5 pentane diol, 3-methylpentane-1,5-diol, hexane diol, oxyalkylated hydroquinone, resorcinol and bisphenol A, hydrogenated bisphenol A, 1,4-cyclohexane dimethanol, polyalkylene oxide diols with molecular weights between 100 - 500, diethyltoluene diamine, ethylene diamine, 10 4,4'-methylene bis(2-chloroaniline) ("MOCA"), hydrazine, substituted aromatic diamines, N,N-bis(2-hydroxypropyl)-aniline, and combinations thereof.

10. The elastomer of claim 7 characterized in 15 that said elastomer additionally contains at least one compounding ingredient selected from the group consisting of anti-oxidants, plasticizers, uv stabilizers, adhesion promoters, fillers and pigments and employed in an amount of between 0 and about 75 20 weight percent based upon the total weight of the composition.

11. The elastomer of claim 7 characterized in that said first polyol has a molecular weight of between 1,500 and 4,000 and said polyol blend has a 25 polydispersity of between 1.1 and 1.5.

12. The elastomer of claim 7 characterized in that said polyol blend has an average ethylene oxide content of less than 35 weight percent if the average molecular weight of said polyol blend is less than 4,000.

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13. A method of fabricating a thermoplastic elastomer characterized by the steps of:

- 5 (a) fabricating a polyol blend of polyether polyols comprising a first polyol and a second polyol, the first polyol being prepared utilizing a double metal cyanide complex catalyst and having a molecular weight of between about 1,000 and about 5,000, said first polyol having an end group unsaturation level of  
10 no greater than 0.04 milliequivalents per gram of polyol, the second polyol being a polyether polyol having an average molecular weight of between about 1,000 and about 20,000, the second polyol being present in an amount of between  
15 about 5% and about 50% based upon the weight of said polyol blend, with the proviso that the average molecular weight of said second polyol is different from the average molecular weight of said first polyol, and with the additional proviso that the polydispersity of said polyol blend is greater than the polydispersity of said first polyol, the polydispersity of said polyol blend being between 1.09 and about 3.0,
- 20 (b) reacting said polyol blend with a diisocyanate to produce an isocyanate-terminated prepolymer, and
- 25 (c) reacting said isocyanate-terminated prepolymer with a difunctional isocyanato-reactive chain extender in a mold or  
30 in an extruder in order to produce a hard elastomer characterized by a hardness of between a 75 Shore A and about a 75 Shore D, with the proviso that when the molecular weight of the

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polyol is less than 4,000, then the polyol blend has an ethylene oxide content of less than 35 weight based upon the weight of the polyol.

14. The method of claim 13 characterized in that said chain extender is selected from the group consisting of diols, diamines, and combinations thereof.

15. The method of claim 13 characterized in that said chain extender is selected from the group consisting of ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, butane diol, pentane diol, 3-methylpentane-1,5-diol, hexane diol, oxyalkylated hydroquinone, resorcinol and bisphenol A, hydrogenated bisphenol A, 1,4-cyclohexane dimethanol, polyalkylene oxide diols with molecular weights between 100 - 500, diethyltoluene diamine, ethylene diamine, 4,4'-methylene bis(2-chloroaniline) ("MOCA"), hydrazine, substituted aromatic diamines, N,N-bis(2-hydroxypropyl)-aniline, and combinations thereof.

16. The method of claim 13 characterized in that said first polyol has a molecular weight of between 1,500 and 4,000 and said polyol blend has a polydispersity of between 1.1 and 1.5.

17. The method of claim 13 characterized in that said elastomer additionally contains at least one compounding ingredient selected from the group consisting of anti-oxidants, plasticizers, uv stabilizers, adhesion promoters, fillers and pigments.

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18. The method of claim 17 characterized in that said compounding ingredient is employed in an amount of between 0 and about 75 weight percent based upon the total weight of the composition.

5 19. The method of claim 13 characterized in that steps (b) and (c) are conducted simultaneously.

20. The method of claim 13 characterized in that said hardness is between an 80 Shore A and a 65 Shore D.

10 21. A "one-shot" process for producing a thermoplastic polyurethane or polyurea elastomer which comprises reacting a polyol blend of polyether polyols comprising a first polyol and a second polyol, a diisocyanate, and a difunctional, isocyanato-reactive  
15 chain-extender, the first polyol being prepared utilizing a double metal cyanide complex catalyst and having a molecular weight of between about 1,000 and about 5,000, said first polyol having an end group unsaturation level of no greater than 0.04  
20 milliequivalents per gram of polyol, the second polyol being a polyether polyol having an average molecular weight of between about 1,000 and about 20,000, the second polyol being present in an amount of between about 5% and about 50% based upon the weight of said  
25 polyol blend, with the proviso that the average molecular weight of said second polyol is different from the average molecular weight of said first polyol, and with the additional proviso that the polydispersity of said polyol blend is greater than the polydispersity of  
30 said first polyol, the polydispersity of said polyol blend being between 1.09 and about 3.0, the equivalent



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ratio of NCO groups on said diisocyanate to active hydrogen groups on said polyol plus chain extender being between about 1:0.7 and about 1:1.3, and the molar ratio of chain extender to polyol being between about 0.15:1 and about 75:1, said elastomer having a hardness of between a 75 Shore A and about a 75 Shore D.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US93/04785

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) : C08G 18/10, 18/48, 18/28

US CL : 528/61, 63, 64, 65, 76

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 528/61, 63, 64, 65, 76

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,379,904 (EHRlich) 12 APRIL 1983 See claims 1, 3 and Examples.	1-21
Y	US, A, 5,096,993 (SMITH) 17 MARCH 1992 See column 2, lines 67-68 and column 3, lines 1-4.	1-21

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be part of particular relevance	X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
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*P* document published prior to the international filing date but later than the priority date claimed		

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